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(Commemoration Issue Dedicated to
Professor Rempei Gotoh On the Occasion of
his Retirement)

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Infrared Spectra of Acetic Acid Adsorbed on Alumina in Carbon Tetrachloride*

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Infrared spectra of acetic acid and deuterated acetic acid adsorbed on alumina were observed at various concentrations in carbon tetrachloride. The adsorption isotherm was of the Langmuir type at relatively low concentrations. When the initial concentration was low, both acetic and deuterated acetic acids were adsorbed on γ -alumina in two kinds of ionic states, characterized by two pairs of absorption frequencies at 1590 and 1465 cm^{-1} and 1560 and 1420 cm^{-1} , while the molecular adsorption was found to proceed as the monomolecular saturation was approached. β -Alumina showed the similar behaviors of adsorption although its adsorbing power was weaker than that of γ -alumina. These results were compared with those obtained by other authors for the adsorption from gaseous states. It was also found that the scattering of radiation by powder was remarkably reduced in the liquid-solid system, which revealed higher accuracy of measurements than in the gas-solid system.

INTRODUCTION

Since 1950, a number of studies have been made of the infrared spectra of adsorbed molecules on solid surface.¹⁾ However, almost all of these studies have dealt exclusively with gas-solid interfaces and the papers dealing with liquid-solid interfaces have been limited in number. But the importance of the study of the adsorbed molecules in liquid-solid interfaces has sufficiently been recognized in the field of colloid and surface chemistry, because they play a major role in the phenomena concerning the surface treatment of powders, suspension of powders, lubrication, dyeing, etc.

In order to study the adsorbed states in liquid-solid interfaces, the infrared spectra of acetic acid and deuterated acetic acid adsorbed on γ - and β -alumina were observed at various concentrations in carbon tetrachloride, and changes in the intensity and shape of the absorption bands were examined in connection with changes in the amount of the adsorbed molecules. The results obtained were discussed referring to those by Peri *et al.*²⁻⁵⁾ on the surface structure of γ -alumina and to those by Shindo *et al.*⁶⁾ on the infrared spectra of formic acid adsorbed on alumina in gaseous phase.

It was also found that the scattering of radiation by powder was remarkably

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reduced in the liquid-solid system, which revealed higher accuracy of measurements than in the gas-solid system.

EXPERIMENTAL

1. Samples

The samples used in this study were γ - and β -alumina prepared by the following procedures. First of all, the precipitate of aluminium hydroxide was obtained by hydrolysis of aluminium isopropoxide (purified by vacuum distillation) in isopropyl alcohol. After washing and drying, the powder was heated at 400–500°C for five hours in an electric furnace. Then it was crushed in an agate moter to pass it through a 300-mesh screen, and was dried at 105°C for three hours. The alumina powder thus obtained was found to have the γ -type crystal structure by means of the x-ray diffraction study. The saturated amount of adsorption on the powder was estimated at 124 mg/g at 25°C from the relation between the amount of the adsorbed molecules and the equilibrium concentration obtained as described below. Assuming that this value corresponds to the amount of monomolecular adsorption and that the cross section of an adsorbed acetic acid molecule is 50 Å,^{2,7)} the specific surface area of γ -alumina can be estimated at 155 m²/g. By heating the sample of γ -alumina at 900°C for five hours, it was transformed into β -alumina, whose structure was confirmed by the x-ray diffraction study.

After dehydration by phosphorous pentoxide, acetic acid used was purified by repetition of distillation and recrystallization.

Deuterated acetic acid (CH₃COOD) was prepared by hydrolysis of pure acetic unhydride in heavy water 80°C in a sealed glass tube and then purified by distillation using a drying tube. The sample obtained was found to be pure CH₃COOD with the aid of the infrared spectrum.

2. Measurements

All the experiments were carried out in a room of constant temperature at 25°C. The alumina sample was added by a ratio of 10 g/l to the solution of acetic acid or deuterated acetic acid in carbon tetrachloride at various concentrations less than 0.1 mol/l. The amount of acetic acid adsorbed on alumina was estimated infrared spectroscopically from the difference in concentration between the initial and equilibrium states of the solution using the absorption band at 1710 cm⁻¹ due to the C=O stretching vibration of acetic acids. The calibration curve used in this estimation is shown in Fig. 1, where A is the absorbance of the C=O stretching band and d the thickness (in cm) of the absorption cell used.

For the measurements of the infrared spectra of the adsorbed molecules, the sedimented alumina in the solution was put into the absorption cell of about 0.1 mm thickness using an injector. In order to compensate the absorption of the solution, the liquid obtained by decantation was put in the absorption cell of the same thickness and was placed in the reference beam of the spectrophotometer. Thus we could record the spectra of the adsorbed molecules as well as of alu-

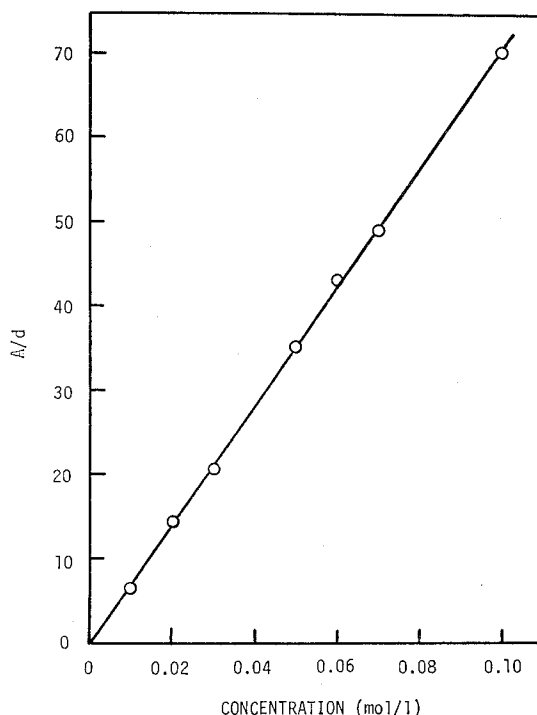


Fig. 1. Calibration curve for the absorption band at 1700 cm^{-1} of acetic acid.

mina without interference due to the absorption of the solution. The infrared spectra were recorded by a Japan Spectroscopic Company Model DS-301 spectrophotometer equipped with two rock salt prisms.

In the infrared measurements of the adsorbed molecules in the liquid-solid system, the scattering of radiation by powder could be reduced remarkably as compared with the case of the adsorption in the gas-solid system.

EXPERIMENTAL RESULTS FOR γ -ALUMINA

1. Time dependence of adsorption

The time dependence was studied for the amount of the adsorbed molecules on γ -alumina after it was added as described above to the acetic acid solution of various concentrations. The results obtained for the case of the initial concentration 0.06 mol/l are shown in Fig. 2 as an example. The rate of adsorption was very high at the initial state and then gradually decreased, the amount of adsorbed molecules attaining to an equilibrium value within *ca.* 20 hours. No change of the amount was found thereafter. Therefore, it is conceivable that the equilibrium of adsorption can be completed at least within 24 hours after the addition of alumina in the solution.

2. Adsorption isotherms

When the amount of the adsorbed molecules was plotted against the equilibrium concentration of the solution, the Langmuir type adsorption isotherm

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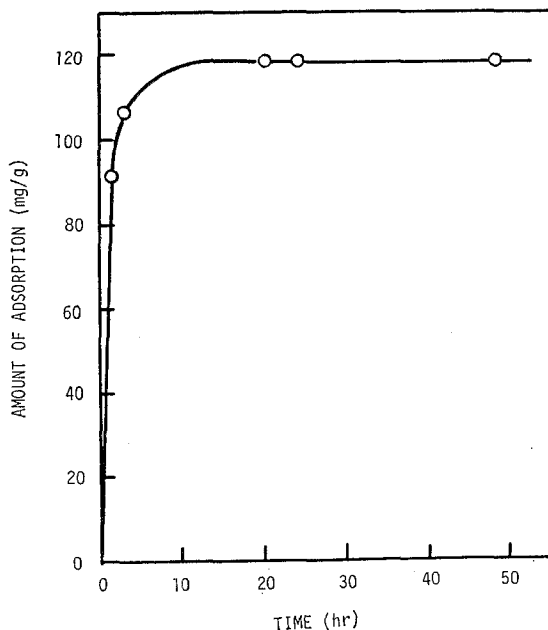


Fig. 2. Time dependence of the amount of acetic acid adsorbed on γ -alumina (25°C).

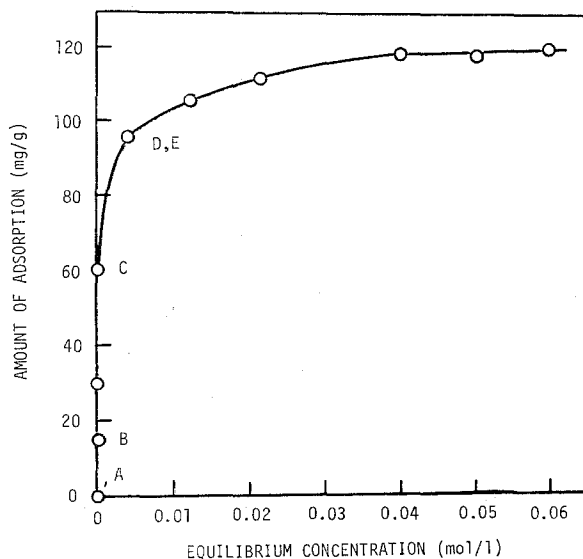


Fig. 3. Adsorption isotherm of acetic acid adsorbed on γ -alumina (25°C).

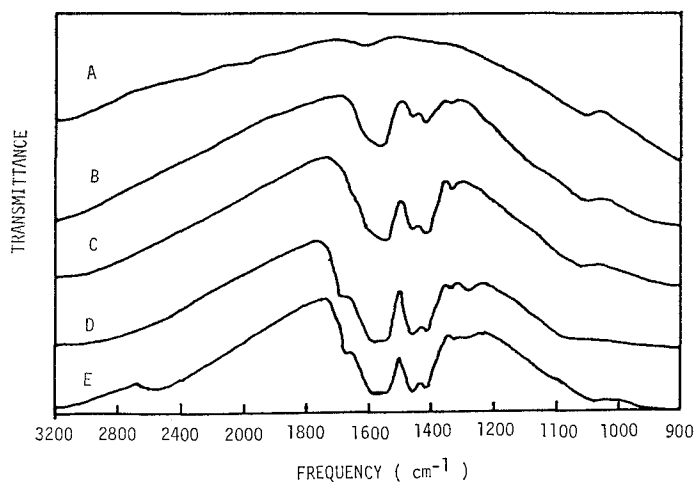
shown in Fig. 3 was obtained in the range of the initial concentration from 0 to 0.1 mol/l. Apparently, the amount of adsorbed acetic acid reached nearly to the saturated value *ca.* 120 mg/g at the equilibrium concentration 0.04 mol/l. Furthermore, when the initial concentration was less than *ca.* 0.01 mol/l, almost all of acetic acids in the solution were adsorbed on the surface of alumina (the amount of the adsorbed molecules was less than 60 mg/g) and therefore the equilibrium

concentration was nearly zero.

3. Infrared spectra of adsorbed molecules

Figure 4 represents the infrared spectra of the molecules adsorbed by various amounts on alumina. The spectra A to E in this figure correspond to those of the adsorption states shown by the same symbols in Fig. 3. The spectra A, B, and C are those in the case of the initial concentration 0, 0.0025 and 0.01 mol/l, respectively. The amounts of the adsorbed molecules at B and C were 15 and 60 mg/g, respectively. In the spectrum B, the absorption bands were found at 1590, 1560, 1465, 1420, and 1340 cm^{-1} where absorptions were observed neither in the spectrum of acetic acid in the solution nor in the spectrum of alumina itself. Although, the spectrum C bore some resemblance to the spectrum B, the relative intensity of the 1590 cm^{-1} band to the 1560 cm^{-1} band was slightly higher in the spectrum C than in the spectrum B and the same was found for the relative intensity of the 1465 cm^{-1} band to the 1420 cm^{-1} band. The spectra of deuterated acetic acid adsorbed on γ -alumina under the initial concentration at 0.0025 and 0.01 mol/l were the same as the spectra B and C, respectively.

The spectra D and E are those of acetic acid and deuterated acetic acid, respectively, adsorbed on γ -alumina under the initial concentration at 0.02 mol/l. In both cases, the amount of adsorption and the equilibrium concentration were 96 mg/g and 0.004 mol/l, respectively. In the spectrum D, the intensity of the 1590 cm^{-1} band was stronger than that of the 1560 cm^{-1} band, and the intensity of the 1465 cm^{-1} band was stronger than that of the 1420 cm^{-1} band. Furthermore, new absorption bands were found in the spectrum D at 1700 and 1285 cm^{-1} where no band was observed in the spectra B and C. Besides these changes in the spectrum D, a broad band appeared at 2500 cm^{-1} in the spectrum E. An



Initial concentration mol/l (Amount of adsorption mg/g)

A: 0 (0), B: Acetic acid 0.0025 (15), C: Acetic acid 0.01 (60)

D: Acetic acid 0.02 (96), E: Deuterated acetic acid 0.02 (96)

Fig. 4. Infrared spectra of acetic acid and deuterated acetic acid adsorbed on γ -alumina.

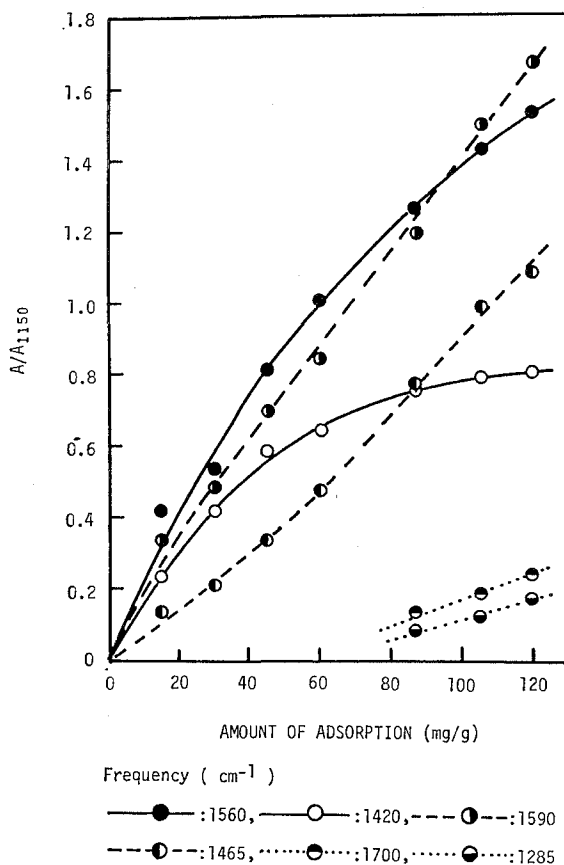


Fig. 5. Relation between the amount of adsorption and absorbance of the bands of acetic acid adsorbed on γ -alumina.

additional change of the spectra could not be found when the concentration of acetic or deuterated acetic acid was increased.

Figure 5 shows the relation between the amount of adsorption and the absorbance (A) of the characteristic bands of the adsorbed molecules. Since, in this case, the sedimentation volume of γ -alumina decreased with increasing surface coverage A/A_{1150} was used as ordinate in Fig. 5, to correct the change of the amount of γ -alumina in the cell with change of the concentration of acids. Here, A_{1150} is the absorbance at 1150 cm^{-1} , where there is no absorption band of the adsorbed molecules but that of alumina itself. Apparently, the curves for the 1560 cm^{-1} band and the 1420 cm^{-1} band exhibited a tendency to saturation, while those of the 1590 cm^{-1} band and the 1465 cm^{-1} band showed the straight lines or an upward tendency. The absorption bands at 1700 and 1285 cm^{-1} appeared at the amount of adsorption 60 mg/g and linearly increased their intensities thereafter.

DISCUSSIONS

In the previous section, it was shown that the absorption bands at 1590 and

1465 cm^{-1} and those at 1560 and 1420 cm^{-1} changed their intensities as respective pairs with the change of the amount of adsorption. Furthermore, it is apparent that the wavenumbers 1590 and 1560 cm^{-1} are close to those of the antisymmetric C=O stretching vibration (1590 cm^{-1}) in aluminum salts of fatty acid and that the wavenumbers 1465 and 1420 cm^{-1} are close to those of the symmetric C=O stretching vibration (1450 cm^{-1}) in the same salts.⁹⁾ These facts suggest that acetic acid is adsorbed on γ -alumina in two kinds of anionic species, one of which (species I) is characterized by the absorptions at 1590 and 1465 cm^{-1} , and another (species II) by the absorptions at 1560 and 1420 cm^{-1} . Although the interpretation of the difference between species I and II is a matter of further studies, it may be desirable to discuss it in connection with the results by Peri *et al.*²⁻⁵⁾ on the surface structure of alumina, who have pointed out that there are five kinds of active sites of adsorption *i. e.* five types of isolated hydroxyl ions differing in the number of oxide ion nearest neighbors. The absorption band at 1340 cm^{-1} observed in the spectra B to E can be assigned to the symmetric CH_3 deformation vibration of acetic acid anions.⁹⁾

The new absorption bands at 1700 and 1285 cm^{-1} found in the spectrum D are attributable to the C=O stretching vibration and the coupled vibration of the OH bending and C—O stretching of acetic acid, respectively.^{10,11)} Therefore, the spectrum D suggests that in the state of adsorption where the surface coverage is close to unity, the anionic species II becomes predominant over species I, and at the same time the physical or molecular adsorption of acetic acid takes place. This is confirmed by the fact that the broad band assignable to the OD stretching vibration was found at *ca.* 2500 cm^{-1} in the spectrum E. The fact that the absorption band due to the OH stretching vibration of acetic acid was not observed in the spectrum D can be understood by considering that the band overlapped with that of alumina itself.

RESULTS AND DISCUSSION FOR β -ALUMINA

The same type of study as that mentioned above was carried out for β -alumina. Figure 6 illustrates the adsorption isotherm obtained for this sample. Apparently, the amount of acetic acid adsorbed on β -alumina reached to saturation at the equilibrium concentration 0.02 mol/l. The saturated value was *ca.* 30 mg/g *i. e.* approximately one fourth of that in the case of γ -alumina. The infrared spectrum of the adsorbed molecules in this case was essentially identical with the spectrum D in Fig. 4. The relation between the amount of adsorption and the absorbance for the bands of acetic acid adsorbed on β -alumina is shown in Fig. 7. The absorption bands at 1560 and 1420 cm^{-1} and those at 1590 and 1465 cm^{-1} behaved as respective pairs as in the case of γ -alumina. It was also found that, in low concentration of acetic acid, they were adsorbed mainly in the form of the anionic species I, and the contribution of the species II to the system increased with increase of the amount of adsorption. On the other hand, the absorption bands at 1700 and 1285 cm^{-1} due to the physical adsorption of acetic acid appeared at the beginning of adsorption in this case while they appeared at the 60 mg/g adsorption in the case of γ -alumina.

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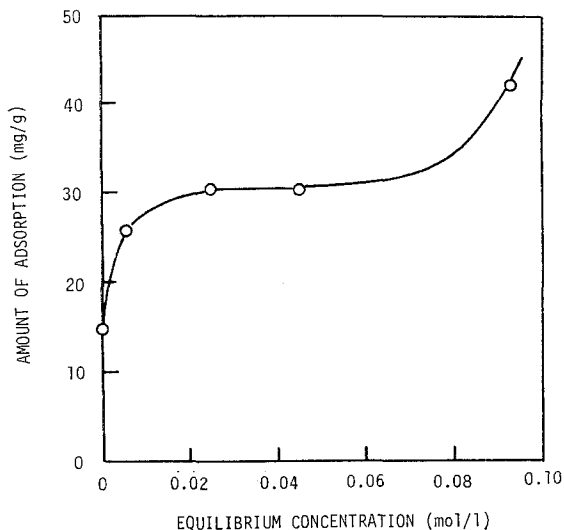


Fig. 6. Adsorption isotherm of acetic acid adsorbed on β -alumina.

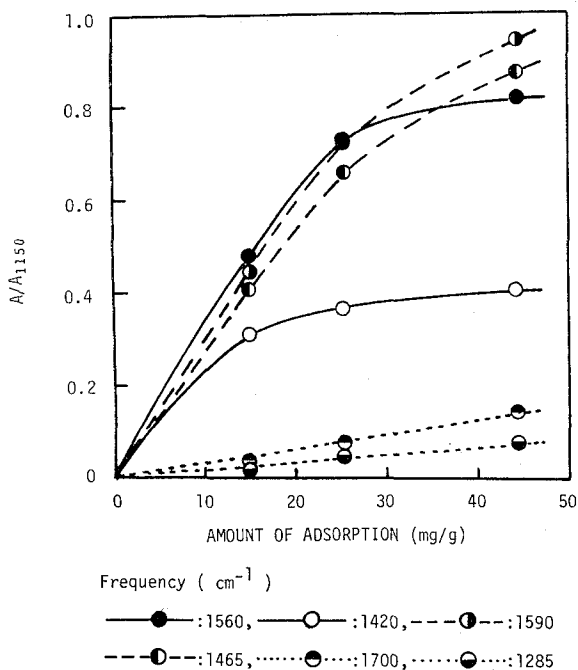


Fig. 7. Relation between the amount of adsorption and absorbance of the bands of acetic acid adsorbed on β -alumina.

It is likely that the differences in the amount of adsorption and in the starting point of the physical adsorption between γ - and β -alumina are ascribed to the difference in the crystal structure or in the amount of surface hydroxyl groups.

Previously, Shindo *et al.*⁶⁾ have studied the infrared spectra of formic acid

adsorbed on alumina from gaseous phase and have stated that the chemisorption in the form of acetic acid anion takes place at the coverage less than unity and that, besides the chemisorption, the physical adsorption in the form of acetic acid takes place at the coverage higher than unity. The results by the present authors are in fairly good agreement with theirs, in spite of the fact that the former was obtained in the liquid-solid system and the latter in the gas-solid system. It is accordingly concluded that the presence of carbon tetrachloride as a medium gives little effect on the state of adsorption of acetic acid on alumina.

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